A Regression Analysis on Tribological Properties of Cerium Oxide-Engine Oil: Effects of Nanoparticles Concentration

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Abstract

Engine Oil is used as a lubricant in automotive engines. It's thermophysical properties can be enhanced upon addition of nanoparticles into it in certain proportions so that the performance of the engine and its durability are increased. This research incorporates cerium oxide nanoparticles in different proportions into SAE 20W40 grade engine oil experimentally as per the standards of the American Society for Testing and Materials, and then evaluates the data collected in statistical software Design Expert used in Design of Experiments. The results showed that the mixture of engine oil with 0.7 wt % cerium oxide nanoparticles had the highest viscosity index, minimum pour point, and an in-range flash point producing an overall desirability factor of approximately 0.90. This could lead to increased efficiency, reduced maintenance costs, and longer engine lifespan.

Keywords: Engine Oil, Nanoparticles, ANOVA, Regression Analysis

Introduction

An automotive engine is an assembly of multiple moving parts which collectively serve to power the automobile. Frictional losses between the moving components of an engine contribute to around 15% of energy losses (Vadiraj et al., 2012). This energy loss affects the engine efficiency adversely. Overheating of the frictional surfaces may also lead to engine breakdown. Lubrication is the process of the use of an oily or greasy material implied at improving the smoothness of motion of one surface over another. Various kinds of lubrications are used in order to diminish the decrementally baneful effects of friction, reduce wear and hence overcome problems related to overheating and corrosion (Lansdown, 2013).

An ideal lubricant should have a high viscosity, high flash point (temperature at which an ignitable mixture forms over the surface of engine oil, at that point the oil will catch fire), while a lower value of pour point (temperature at which the lubricant loses its flow characteristics and clots, resulting in increase in the resistive frictional

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forces). Besides, it should be thermally stable, high resistance to surface oxidation as well as provide prevention against corrosion (Devlin, 2018).

Inside the engine of an automotive, engine oil serves two purposes: As a lubricant between the sliding parts and as a coolant where it takes away the exhorbitant heat from the mobile components inside the engine machinery. The excessive heat stored in the bulk of the lubricating fluid decreases its viscosity. Consequently, the lubricating layers' thickness is reduced which in turn results in a higher rate of friction and wear between the moving surfaces inside the engine (Dinesh et al., 2016). Hence, conventional lubricants tend to become ineffective over the course of time and result in overheating of the car engine. The viscosity of a lubricating fluid decreases with increase in temperature and pressure (Devlin, 2018; Lansdown, 2013). Viscosity Index (VI) is the most commonly used indicator to define the effect of temperature on viscosity of the lubricant. Lubricants with very low VI become thin at high temperatures, which reduces their ability to reduce friction and wear. On the other hand, a high VI is also not desirable since this results in agglomeration and restricts the lubricant flow (Verdier et al., 2009).

Choi (Wang et al., 2013) proposed that the cooling capability of lubricants can be enhanced by introduction of nanoparticles of high thermal conductivity materials in coolants. This mixture of nanoparticles in fluids like oil is termed as nanofluids (Esfe et al., 2018). Nanoparticles are being used extensively in the field of material science since they are easier in portability and economic in cost. *Esfe et al.* (Esfe et al., 2018) have reported that if the nanoparticles suspended in the fluid have high thermal conductivity, the combination results in improved heat transfer properties of the engine oil, thus increasing the performance of engine.

In this study, the tribological properties, i.e. friction and wear losses in automotive engines, are addressed by improving the heat transfer properties of engine oils. The most well-known way of improving engine oil properties is through the incorporation of a small amount of additives. In the following paragraphs, the relevant research with the incorporation of the nano particle has been provided

Thottackked et al. (Thottackkad et al., 2012) reported that addition of Copper Oxide nanoparticles (Nallusamy, 2016) in coconut lube improved the wear and friction coefficient. Besides, proliferation of nanomaterials in the base oil also increased the viscosity. *Laad et al.* (Laad & Jatti, 2018) used nano-particles of Titanium Oxide as supplement in engine oil; the results of this study also showed an enhancement in the tribological characteristics of engine oil. *Dinesh et al.* (Dinesh et al., 2016) studied the effect of incorporating carbon nanotubes (CNTs) and Zinc Oxide nano-particles in engine oil. The results showed that addition of nanoparticles in engine oil enhanced the thermal conductivity, kinematic viscosity and flash point of the oil consdierably. Similarly, *Esfe et al.* (Esfe et al., 2018) also dispersed carbon nanotubes (CNTs) and Zinc Oxide nano-particles in SAE 5W50 grade engine oil and reported that VI of the resulting mixture improved sufficiently i.e. viscosity reduction. This consequently, diminished the mechanical deterioration in the engine caused by cold start condition.

Vadiraj et al. (Vadiraj et al., 2012) deduced that by addition of copper nanoparticles in engine oil, the drag between moving components of the engine and the oil (surface-to-surface contact) reduced in number, thereby diminishing the wear damage due to friction. *Wu et al.* (Wu et al., 2007) investigated the effect of addition of Copper nano-particles on the tribological properties of API-SF engine. It was noted that the friction coefficient decreased by 5.8% thereby improving the anti-wear characteristics of the engine oil.

Although the literature reported above shows promising results but the issue of long term stability of nano fluids remains a concern. *Ahmadi et al.* (Ahmadi et al., 2013), *Ma et al.* (Ma et al., 2020), and *Thottacked et al.* (Thottackkad et al., 2012), argue that a vast majority of oil based nanofluids bid a sound refinement in thermal conductivity, flash point, pour point, viscosity Index, tribological properties etc., they lack long term stability. Hence there is a need to develop durable nanofluids. This can be achieved by introduction of more stable nano-particles.

Unlike metallic counterparts, metal oxide nanoparticles such as cerium oxide (CeO_2) nanoparticles (Sreeremya et al., 2014) have relatively greater chemical stability over long duration of time. In addition, they are not vulnerable to surface oxidation. These technically encouraging elements along with low electrical conductivity, huge improvements in viscosty index, pour point, flash point, and long-term suspension stability, make cerium oxide nanomaterial a palausible choice for application in engine oil. The work reported in this paper investigated the effect of different blends of CeO_2 nanoparticles in engine oil. This was followed by optimization and selection of the most desirable nanofluid using State-Ease: Design Expert Software.

Material and Methods

The methods and materials that are used in research and the properties that are the objectives of the study are explained here. It includes the experimental setup, sample preparation and experimental process that is discussed here with detail. The viscosity index, pour point and flash point are discussed as well.

Experimental Setup

Sigma-Aldrich's Cerium (IV) oxide nano-powder of 10 nm to 30 nm in size were used in current study. In addition, the experimental setup consisted of a gasoline powered 125 cc Internal Combustion Engine and Engine oil having SAE grade 20W40. The specifications of other measuring devices/apparatuses are given below:

(a) *Viscometers:* Two types viscosity measuring instruments were used measuring viscosity at 40°C and and other at 100°C. Specification of both the viscometers are given as under:

TYPE 1: for 40°C	Ubbelhode viscometer
Marked:	PSL ASTM-IP 2C
Constant:	0.3146 (mm^2/s)/s

TYPE 2: for 100°C	Ubbelhode viscometer
Marked:	PSL ASTM-IP 1B
Constant:	0.5252 (mm^2/s)/s

(b) *Flash Point and Pour Point Measuring Apparatus:* The device is used to measure the flash point and pour point of lubrication oil. Specification are as follow:

Type:	Petrotest D-15827
Method:	ASTM D97

(c) *Ultrasonicator:* This device is used for mixing of cerium oxide nano particles in the engine oil through ultarasonic bath or by ultrasonic waves.

Type:	Ultrasonic bath
Model:	Power Sonic 410

Preparation of Nanofluid

Three samples each of one-liter capacity, containing different concentration of CeO_2 nanoparticles where prepared through ultrasonication, at at PCSIR Laboratory, Peshawar. The sample concentrations devised were as follows:

- **(a)** Sample I: Engine Oil+0 wt% CeO_2 nanoparticles
- **(b)** Sample II: Nanofluid Engine Oil + 0.1 wt% CeO_2 nanoparticles
- **(c)** Sample III: Nanofluid Engine Oil + 0.3 wt% CeO_2 nanoparticles
- **(d)** Sample IV: Nanofluid Engine Oil + 0.7 wt% CeO_2 nanoparticles

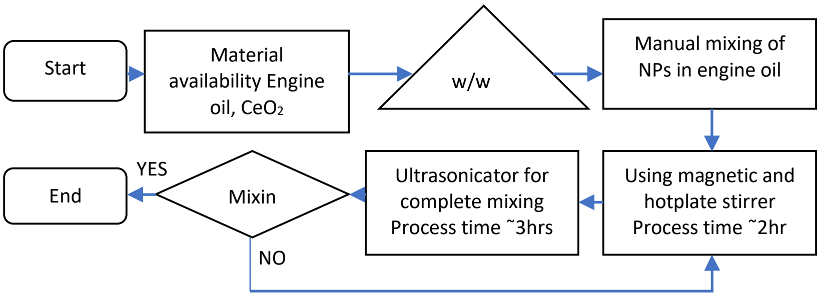


Figure 1: Sample Preparation Flow Chart

Figure 2: Sample Preparation using Ultra-sonification (Front View)

The Viscosity Index, Pour Point, and Flash Point were measured for the base engine oil before the test. The engine was then operated for 10 hours at different RPMs and the same data was collected for the sample. Similarly, different samples of nano-fluid containing 0.1 wt%, 0.3 wt%, and 0.7 wt% CeO2 nanoparticles were prepared, and similar data were measured for the samples of engine oil, both before and after the engine was operated for 10 hours at different RPMs.

The ASTM standard methods are used for the collection of data in the experiments. The following ASTM methods are used:

- **(a)** ASTM D445: for measuring the Kinematic viscosity of oil at 40°C and 100°C.
- **(b)** ASTM D2270: for aid in calculation of Velocity Index using Tables.
- **(c)** ASTM D97: for measuring the Pour point of engine oil.
- **(d)** ASTM D92: for measuring the Flash point of engine oil.

The Viscosity Index (VI) is calculated using ASTM D2270 standard using following mathematical formula :

$$VI=100\ \frac{(L - U)}{(L - H)}$$

where: VI is the Velocity Index U is the oil's kinematic viscosity at 40°C. The above equation involves comparing the viscosity of the lubricant at both high (H) and low (L) temperatures to a reference oil.

The calculation takes into account the kinematic viscosities of the lubricant at 40°C and 100°C and uses these values to determine the VI.

Experiment and Analysis

The temperature data was obtained by reading it off the apparatus, and the Viscosity Index was calculated using the above equation. The calculated data for the Viscosity Index, as well as the measured data for the Flash Point and Pour Point, are presented in Table 1 below.

Statistical Analysis:

The statistical software Design Expert, Version 12 has been used in the study for analysis of the data. It is used for comparative analysis, characterization, design and optimization of an experimental problem; and then analysis of variance (ANOVA) to link the factors involved and evaluate the p-values based upon which the conclusions were drawn(Onoghwarite et al.).

Table 1

Viscosity Index, Pour Point and Flash Point

	Engine oil (0% nano-particles)		**Engine oil (0% nano-particles)**		**Nanofluid (0.3 wt% nano-particles)**		**Nanofluid (0.7 wt% nano-particles)**	
	Before	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**
Viscosity index	105.63	88.31	105.72	100.54	106.36	104.68	109.70	111.03
	107.74	90.08	107.83	102.55	107.96	106.25	111.35	112.70
	104.04	86.99	105.56	100.39	107.05	105.36	110.41	111.75
	105.89	88.53	105.98	100.79	106.31	104.63	109.65	110.98
	105.47	88.18	105.56	100.69	102.64	101.02	105.86	107.14
Pour point (°c)	-9	-11	-2	-9	-3	-9	-3	-13
	-8	-11	-1	-10	-3	-11	-5	-11
	-9	-10	-1	-9	-3	-9	-1	-14
	-9	-12	-2	-8	-2	-11	-3	-13
	-10	-10	-2	-10	-5	-8	-2	-14
Flash point (°c)	222	246	260	254	264	254	260	254
	223	248	262	257	261	251	262	255
	222	245	259	253	266	255	259	253
	220	243	260	255	264	253	261	251
	224	243	260	254	262	252	260	255

The comprehensive data analysis suggests selecting the most optimum sample of engine oil from the prepared set of samples, which will result in improved engine performance. The following are the evaluation model parameters:

Table 2
Factors and their responses

	Name	Units	Min	Max	Mean	Std. Dev.
Factors						
A	Engine Oil		0.0	0.7	0.275	0.2715
B	Engine Test Run	Before - After	-1.0	1.00	0.000	1.01
Response						
R1	Viscosity Index		86.99	112.69	103.98	6.750
R2	Pour Point	deg C	-14	-1	-7.4	4.131
R3	Flash Point	deg C	220	266	251.55	12.557

A fraction factorial design is selected with factor parameter Engine Oil Samples (A), Engine Test Run (B) (Before & After), and Interaction between Engine Oil Samples and Engine Test Run (AB). The model type is two-factor interaction with investigation of responses Viscosity Index (R1), Pour Point (R2), and Flash Point (R3).

Viscosity Index

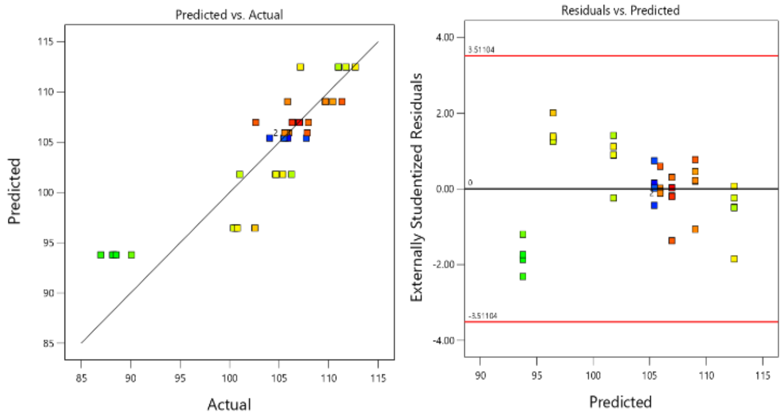
The viscosity of a lubricant is a measure of its resistance to flow, and it is an important factor in determining the performance of a lubricant in various applications, especially in internal combustion engines. A high Viscosity Index indicates that the lubricant's viscosity changes little with changes in temperature, while a low VI indicates that the viscosity changes significantly with temperature.

The analysis of variance (ANOVA) of this model is shown in Table 3 below.

Table 3
ANOVA Table for Viscosity Index

Source	Sum of Squares	Df	Mean Square	F-Value	P-Value	
Model	1389.36	3	463.12	42.96	< 0.0001	Significant
A-Engine Oil	730.66	1	730.66	67.78	< 0.0001	
B-Engine Test Run	155.29	1	155.29	14.40	0.0005	
Ab	333.06	1	333.06	30.89	< 0.0001	
Residual	388.10	36	10.78			
Lack Of Fit	301.58	4	75.39	27.88	< 0.0001	Significant
Pure Error	86.52	32	2.70			
Cor Total	1777.46	39				

As depicted in Table 3, the Model F-value of 89.34, and P-values less than 0.0500 infers that the model and model terms under consideration is to be taken as significant In this case Engine Oil , Engine Test Run, and Interaction between Engine Oil and Test Run are significant model terms. The model has a standard deviation of 1.64 and mean of 103.98. Also, the residual analysis of the model, shown in Figure 3, is satisfactory, with the data points are within the limits of experimental accuracy and no single point lies outside either the lower or upper bounds.



(a) (b)

Figure 3: (a) Predicted vs Actual Diagnostic Curve and (b) Residual vs Predicted Diagnostic Curve for Viscosity Index

The Response Surface

Figure 4 Shows the contour and surface plot for viscosity index. The sample of engine oil containing 0.7 wt% nanoparticles is the best response, as demonstrated by the increased viscosity index by an average of 12.45% compared to other samples. Thus, increased VI indicates that the oil maintains its viscosity over a wider range of temperatures, making it more resistant to changes in viscosity and providing more consistent lubrication. Additionally, it can be observed that the index improved even after running the oil in the engine.

Pour Point

The pour point of a lubricating oil is the temperature at which it stops flowing and becomes too thick. It is an important property, especially in cold climates, where low temperatures can cause oils to thicken and become less effective as lubricants. A lower pour point is preferred in these conditions. Other factors, such as engine requirements and oil formulation, must also be considered when selecting the best lubricating oil. Using the effects and relations, Table 4 shows the ANOVA for selected factorial model.

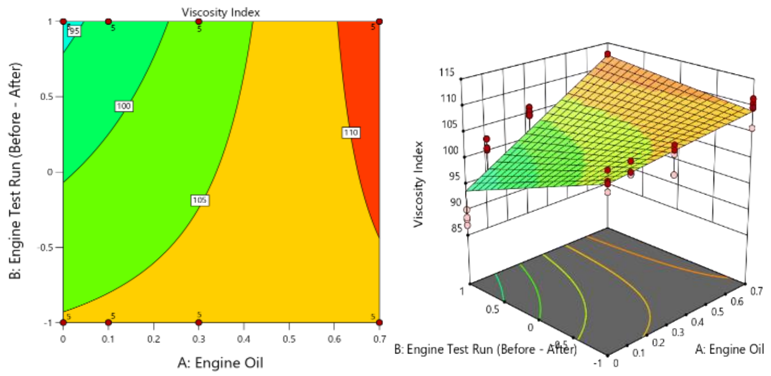


Figure 4: (a) Contour Plot, and (b) 3D Surface for Viscosity Index

Table 4
ANOVA Table for Pour Point

Source	Sum of squares	Df	Mean square	F-value	P-value	
Model	485.27	3	161.76	32.29	< 0.0001	Significant
A-engine oil	0.7826	1	0.7826	0.1562	0.6950	
B-engine test run	480.31	1	480.31	95.89	< 0.0001	
Ab	61.99	1	61.99	12.38	0.0012	
Residual	180.33	36	5.01			
Lack of fit	144.73	4	36.18	32.52	< 0.0001	Significant
Pure error	35.60	32	1.11			
Cor total	665.60	39				

The Model F-value of 80.98, and P-values less than 0.0500 implies the model and model terms are significant. In this case A, B, and AB are significant model terms. The model has a standard deviation of 1.50 and mean of 6.60. Also, Figure 5 show the residual analysis of the model to be satisfactory, as the data points are within the limits of experimental accuracy and no single point lies outside either the lower or upper bounds.

The response Surface

Figure 6 shows the contour and surface plot for pour point. The sample of engine oil containing 0.7 wt% nanoparticles presents the best response, as indicated by the decreased pour point by 22% compared to other. As in case of VI, indicated in section 3.2, there is an increase in its value. A higher VI may also be associated with a higher pour point, which could make the oil more difficult to pump in very cold temperatures. But, the 0.7 wt% nanoparticle sample shows a decrease in pour point, which infact is an improvemtn in the tribological properties of the engine oil.

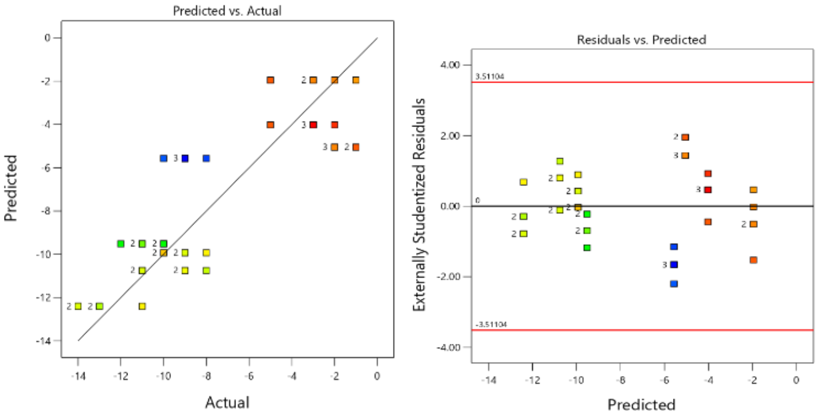
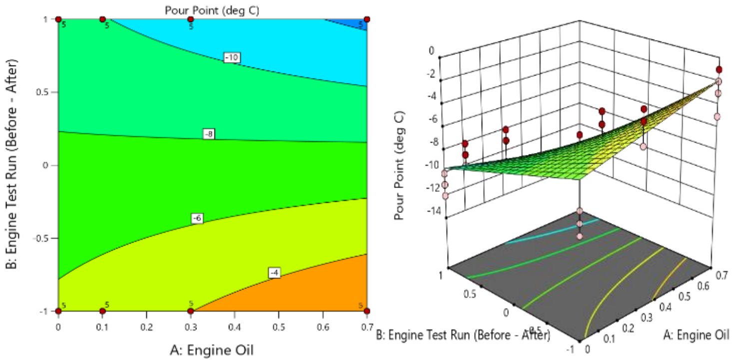


Figure 5: (a) Predicted vs Actual Diagnostic Curve, and (b) Residual vs Predicted Diagnostic Curve for Pour Point



(a) (b)

Figure 6: (a) Contour Plot, and (b) 3D Surface for Pour Point

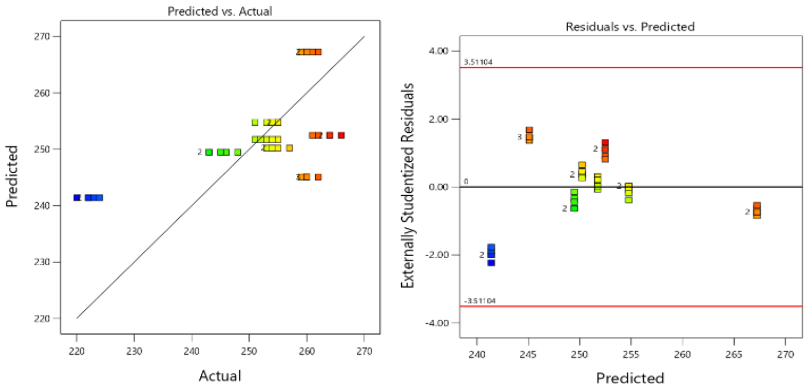
Flash Point

The flash point of engine oil is the temperature at which the oil gives off vapors that can be ignited with a flame, but the oil does not continue to burn once the ignition source is removed. This property of engine oil indicates the temperature at which the oil can ignite and potentially cause a fire or explosion. In general, a higher flash point indicates that the oil is less likely to ignite and is therefore safer to use. The flash point is typically measured using standardized laboratory tests, such as ASTM D92, and is reported in units of degrees Celsius or Fahrenheit. Table 5 shows the ANOVA for selected factorial model.

As depicted in Table 5, the Model F-value of 336.62 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A and AB are significant model terms while B is insignificant model term since the values greater than 0.10000 indicate the model terms are not significant. The model has a standard deviation of 1.60 and mean of 251.55. Figure 7 show the Predicted vs Actual, Residual vs Predicted, and Residual vs Run; diagnostic curves for the parameter of Response 3 i.e. Flash Point.

Table 5
ANOVA Table for Response 3: Flash Point

Source	Sum of squares	Df	Mean square	F-value	P-value	
Model	2041.89	3	680.63	5.96	0.0021	Significant
A-engine oil	1422.47	1	1422.47	12.47	0.0012	
B-engine test run	44.96	1	44.96	0.3940	0.5342	
Ab	619.42	1	619.42	5.43	0.0255	
Residual	4108.01	36	114.11			
Lack of fit	4025.61	4	1006.40	390.84	< 0.0001	Significant
Pure error	82.40	32	2.58			
Cor total	6149.90	39				



(a) (b)

Figure 7: (a) Predicted vs Actual Diagnostic Curve, and (b) Residual vs Predicted Diagnostic Curve for Flash Point

Through inspection of the data presented in Figure 7 it is interpreted that the data points are within the limits of experimental accuracy and no single point lays outside the either of lower or upper bounds. Figure 8 shows the contour and surface plot for flash point. It shows both the before (red) and after (green) response of the respective samples.

The best response is presented by the sample of engine oil containing 0.7 wt% nanoparticles since it has remained the same relatively to other samples.

Numerical Optimization and desirability

In order to select, numerical optimization is performed on the entire data to get the overall desirability. The criterion for the three responses is set as tabulated in Table 6.

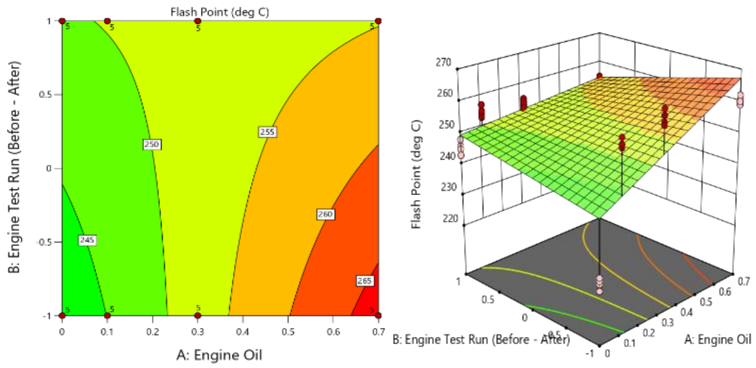
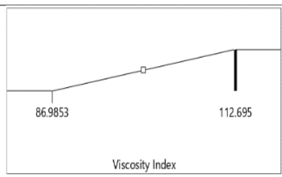
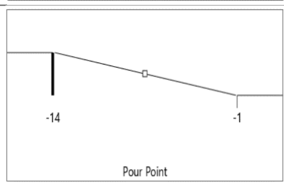
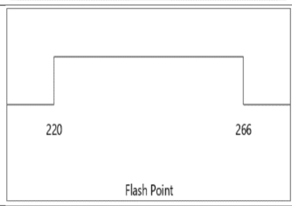


Figure 7: (a) Contour Plot, and (b) 3D Surface for Flash Point

Table 6
Criterion for Numerical Optimization

S.No.	Response	Criteria	Illustration
1.	Viscosity Index	Maximize	
2.	Pour Point	Minimize	
3.	Flash Point	In Range	

The Nanofluid (0.7 wt%) i.e. the sample of engine oil with 0.7 wt % Cerium (IV) oxide nanoparticles incorporated as the most desirable with the desirability factor of 0.923. The desirability factor of Base Oil has been calculated as 0.670 while that of Nanofluid (0.1 wt% nanoparticles) and Nanofluid (0.3 wt% nanoparticles) have come out to be 0.586 and 0.669.

Conclusion

Incorporation of cerium oxide nanoparticles in the engine oil was a difficult task due to the high viscosity of the base oil itself, however, ultrasonification technique aided in the prospective uniform mixing of the nanoparticles in the engine oil to produce different samples of nanofluids. The nanofluid mixtures formed had neither agglomeration nor precipitation. It was noticed that with increase in the concentration of nanoadditives, the thermophysical properties of the engine oil, namely, viscosity index, pour point, and flashpoint improved. In the research under consideration, peoperties of nanofluids were evaluated at three different concentrations. The Stat-Ease Design Expert Software was used for statistical analysis of all the three responses and thus it was determined that the sample of engine oil with 0.7 wt % Cerium (IV) oxide nanoparticles incorporated as the most desirable with the desirability factor of 0.923. The desirability factor of Base Oil has been calculated as 0.670 while that of Nanofluid (0.1 wt% nanoparticles) and Nanofluid (0.3 wt% nanoparticles) have come out to be 0.586 and 0.669.

References

Ahmadi, H., Rashidi, A., Mohtasebi, S. S., & Alaei, M. (2013). Experimental evaluation of engine oil properties containing copper oxide nanoparticles as a nanoadditive. *International Journal of Industrial Chemistry*, *4*(1), 1-6.

Devlin, M. T. (2018). Common Properties of Lubricants that Affect Vehicle Fuel Efficiency: A North American Historical Perspective. *Lubricants*, *6*(3), 68. https://www.mdpi.com/2075-4442/6/3/68

Dinesh, R., Prasad, M. G., Kumar, R. R., Santharaj, N. J., Santhip, J., & Raaj, A. A. (2016). Investigation of tribological and thermophysical properties of engine oil containing nano additives. *Materials Today: Proceedings*, *3*(1), 45-53.

Esfe, M. H., Arani, A. A. A., & Esfandeh, S. (2018). Improving engine oil lubrication in light-duty vehicles by using of dispersing MWCNT and ZnO nanoparticles in 5W50 as viscosity index improvers (VII). *Applied Thermal Engineering*, *143*, 493-506.

Laad, M., & Jatti, V. K. S. (2018). Titanium oxide nanoparticles as additives in engine oil. *Journal of King Saud University - Engineering Sciences*, *30*(2), 116-122. https://doi.org/https://doi.org/10.1016/j.jksues.2016.01.008

Lansdown, A. (2013). *Lubrication: a practical guide to lubricant selection*. Elsevier.

Ma, J., Shahsavar, A., Al-Rashed, A. A., Karimipour, A., Yarmand, H., & Rostami, S. (2020). Viscosity, cloud point, freezing point and flash point of zinc oxide/SAE50 nanolubricant. *Journal of Molecular Liquids*, *298*, 112045.

Nallusamy, S. (2016). Thermal conductivity analysis and characterization of copper oxide nanofluids through different techniques. Journal of Nano Research, Onoghwarite, O. E., Obiora, N. V. I., & Ben, E. A. Journal Homepage:-www. journalijar. com.

Sreeremya, T. S., Krishnan, A., Mohamed, A. P., Hareesh, U., & Ghosh, S. (2014). Synthesis and characterization of cerium oxide based nanofluids: an efficient coolant in heat transport applications. *Chemical Engineering Journal*, *255*, 282-289.

Thottackkad, M. V., Perikinalil, R. K., & Kumarapillai, P. N. (2012). Experimental evaluation on the tribological properties of coconut oil by the addition of CuO nanoparticles. *International journal of precision engineering and manufacturing*, *13*(1), 111-116.

Vadiraj, A., Manivasagam, G., Kamani, K., & Sreenivasan, V. (2012). Effect of nano oil additive proportions on friction and wear performance of automotive materials. *Tribology in Industry*, *34*(1), 3.

Verdier, S., Coutinho, J. A., Silva, A. M., Alkilde, O. F., & Hansen, J. A. (2009). A critical approach to viscosity index. *Fuel*, *88*(11), 2199-2206.

Wang, B., Hao, J., & Li, H. (2013). Remarkable improvements in the stability and thermal conductivity of graphite/ethylene glycol nanofluids caused by a graphene oxide percolation structure. *Dalton Transactions*, *42*(16), 5866-5873.

Wu, Y., Tsui, W., & Liu, T. (2007). Experimental analysis of tribological properties of lubricating oils with nanoparticle additives. *Wear*, *262*(7-8), 819-825.